

Fuel processor integrated H₂S catalytic partial oxidation technology for sulfur removal in fuel cell power plants[☆]

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Abstract

H₂S catalytic partial oxidation technology with an activated carbon catalyst was found to be a promising method for the removal of hydrogen sulfide from fuel cell hydrocarbon feedstocks. Three different fuel cell feedstocks were considered for analysis: sour natural gas, sour effluent from a liquid middle distillate fuel processor and a Texaco O₂-blown coal-derived synthesis gas. The H₂S catalytic partial oxidation reaction, its integratability into fuel cell power plants with different hydrocarbon feedstocks and its salient features are discussed. Experimental results indicate that H₂S concentration can be removed down to the part-per-million level in these plants. Additionally, a power law rate expression was developed and reaction kinetics compared to prior literature. The activation energy for this reaction was determined to be 34.4 kJ/g mol with the reaction being first order in H₂S and 0.3 order in O₂. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Desulfurization; Hydrogen sulfide catalytic oxidation; Fuel cells

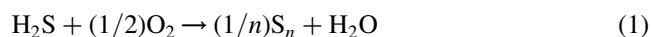
1. Introduction

Principle components in fuel cell power plants including reforming catalysts, anodic electrocatalysts and metallic interconnects are susceptible to sulfur poisoning and require the advancement of integrated, low cost and compact desulfurization technology that can sweeten hydrocarbon feedstocks down to the part-per-billion level.

To date, fuel cell systems have relied mainly on batch operation of sorbent-based technology for sulfur removal. While much of this technology possess the necessary removal efficiency, the low capacity associated with batch

wise operation coupled with the utilization of potentially high sulfur hydrocarbon feedstocks, greatly affect the fuel processor footprint and sorbent maintenance interval.

In an effort to develop a more compact, maintenance free desulfurization system our laboratory has examined utilization of continuous desulfurization technologies. For fuel cell power plants, H₂S selective catalytic partial oxidation is a technology that may prove to be attractive. In addition to being a continuous sulfur removal technology, it has the thermodynamic potential to remove sulfur to the part-per-billion level below 150 °C [1]. The chemistry behind this technology is simple:



Here, free energy minimization calculations [2] have shown that $n = 2, 6$, or 8 depending on the temperature of the reaction. The elemental sulfur product is then easily separated and recovered from the fuel gas as a solid or liquid condensed phase.

In the literature, a number of studies have been conducted on the application of H₂S catalytic partial oxidation technology to the desulfurization of wellhead natural gas [2–6]. Ghosh and Tollefson [6] were the first to examine the applicability of reaction (1) using an activated carbon catalyst to sweeten natural gas. More recent attention

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has turned to the application of this technology to the desulfurization of coal-derived synthesis gas. Meyer et al. [7] reported on an H₂S catalytic partial oxidation entrained reactor system utilizing an activated carbon catalyst. In their system, air was co-injected with activated carbon into the entrained reactor. The elemental sulfur product formed was retained within the micropores of the catalyst that was later recovered downstream in a filtration unit. With liquid fuels, to our knowledge, no research has yet been reported.

It is generally accepted that the structure of activated carbon consists of aromatic sheets and strips with variable gaps that make up a microporous structure [8]. With activated carbon catalysts the sulfur product accumulates in the smallest pore fraction first, due to capillary effects [2]. Correspondingly, since most of the surface area is associated with the smallest micropore fraction, activated carbon catalysts rapidly deactivate through occlusion of active sites. Eventually, the small pore fraction becomes completely filled and a stationary level of activity is reached. In this region, the capillary forces of these pores are insufficient to retain the product sulfur and the rate of H₂S adsorption and reaction equals that of sulfur product desorption.

This gives rise to two possible methods of operation, one in which the elemental sulfur produced is retained as a condensed phase within the pores of the catalyst. Here, thermal regeneration may then be employed to desorb the sulfur product and restore complete activity to the catalyst. The other method of operation is a fully continuous operation, where the rate of H₂S adsorption and reaction equals that of sulfur product desorption.

In the present work, we report on the ability of activated carbon to function as an oxidation catalyst, selectively oxidizing H₂S directly to elemental sulfur. Three different fuel cell feedstocks were considered for analysis: sour natural gas, sour effluent from a liquid middle distillate fuel processor and a Texaco O₂-blown coal-derived synthesis gas. The H₂S catalytic partial oxidation reaction, its integratability into fuel cell power plants with different hydrocarbon feedstocks and its salient features are discussed. The ability for this technology and this catalyst to produce a sweetened fuel cell feedstock is discussed. A power law rate expression was developed to address some of the disparity present in the reaction rate literature. The concepts developed provide the basic information necessary to integrate H₂S catalytic partial oxidation technology into fuel cell power plants.

2. Experimental

2.1. Catalyst properties

The catalyst utilized in this study was Centaur 4 × 6 granular activated carbon obtained from Calgon Carbon Corporation. This activated carbon was manufactured from

Table 1
Properties of activated carbon

Trace metals (ppmg)		Physicochemical properties	
Aluminum	6332	BET surface area (m ² /g)	662
Calcium	795.4	Particle density (g/cm ³)	0.87
Cobalt	15.73	Skeletal density (g/cm ³)	2.07
Chromium	8.281	Particle size (mm)	3.7
Copper	24.16	Porosity (%)	60
Iron	1832	Crush strength (kpsi)	10.7
Phosphorous	32.49	Loss on attrition (%)	10.5
Potassium	422.3	Ash (wt%)	4.93
Magnesium	194.8	Peroxide no. ^a	14
Manganese	3.800	Iodine no. ^a	800
Molybdenum	2.387		
Sodium	313.7		
Nickel	11.64		
Titanium	237.7		
Water (wt%)	4.15		
Zinc	16.61		

^a Provided by manufacturer.

bituminous coal and was known to possess catalytic properties. Table 1 is a compilation of the physicochemical properties of this catalyst. N₂ BET surface area measurements were made according to ASTM D 3663-92 [9] using a Micromeritics Accusorb 2100 E instrument. Catalyst crush strength was measured according to ASTM D 4179-88A [10] and attrition testing was conducted according to ASTM D 4058-92 [11]. Trace metals analysis was conducted using a Varian model 425 atomic absorption spectrometer.

2.2. Experimental apparatus

The experimental apparatus used to conduct this series of experiments was a laboratory scale, quartz fixed bed reactor 1.16 m long by 10.5 × 10⁻³ m in internal diameter. Tightly packed quartz wool was used as a distributor to support the catalyst. Prior to testing, the activated carbon catalyst dried under vacuum at 50 °C to remove residual moisture. Reaction conditions were normalized at a total pressure of 156.5 kPa and GHSV of 2500 h⁻¹.

The reactor was vertically positioned in a Lindburg single zone furnace (model no. 56447) in the down flow mode. Reaction temperature was monitored by a K-type thermocouple located externally at the center of the catalyst bed. Swagelok PFA fittings were used to seal the reactor ends with 1/8 in. Teflon tubing used as a gas sampling line. Temperature control for the reactor was achieved using a Honeywell controller set for constant heat flux output. Details of this arrangement are depicted in Fig. 1.

Gas mixtures were simulated by metering and manifold-ing individual bottled gases supplied by Matheson. The individual gas flow rates were controlled using MKS 1980 thermal mass flow controllers coupled with an MKS model 248C power supply. The composition of the three fuel gases: a Texaco entrained O₂-blown coal-derived fuel gas, a

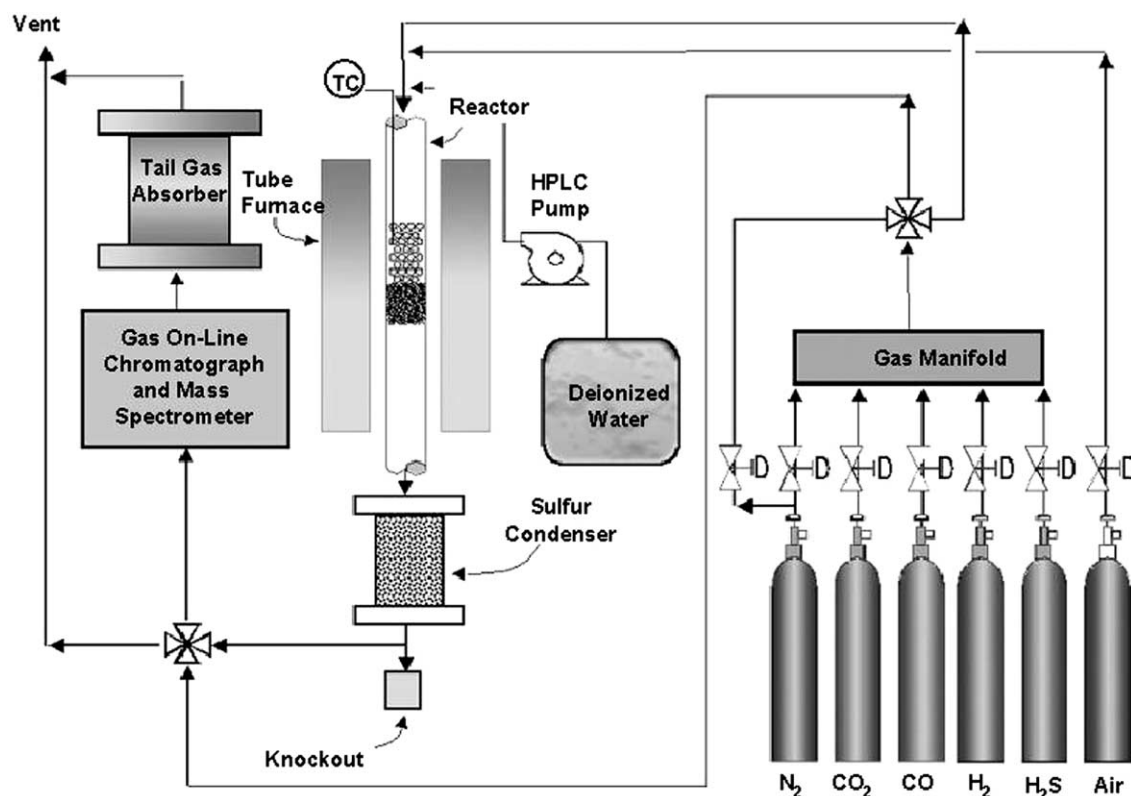


Fig. 1. Experimental setup.

sour natural gas and sour effluent from a liquid middle distillate fuel processor are given in Table 2.

2.3. Analytical methods

Catalyst performance experiments utilized gas chromatography to analyze for H_2S , COS, CS_2 and SO_2 gases at the reactor exit. H_2S was analyzed using a glass column 1/8 in. \times 6 in. packed with (40/60 mesh) Carboxen BHT 100. The column was used in Perkin–Elmer Sigma 300 gas chromatograph equipped with flame photometric detector (FPD). SO_2 was analyzed using a Teflon column 1/8 in. \times 8 in. packed with Chromosil 310. The column was used in a Perkin–Elmer 8500 gas chromatograph equipped with an FPD. COS and CS_2 were analyzed using a Teflon column 1/8 in. \times 8 in. packed with Chromosil 310.

Table 2
Composition of fuel gases tested

Gas content (vol%)	Texaco entrained O_2 -blown coal gas	Pipeline natural gas	HDS liquid middle distillate effluent
CO	35.91	–	–
H_2	26.91	–	78.0
CO_2	12.30	–	–
H_2O	18.05	–	–
N_2	6.73	–	20.5
H_2S	0.10	0.05	1.50
CH_4	–	99.95	–

The column was used in a Perkin–Elmer AutoSystem gas chromatograph equipped with a FPD. The COS, H_2S , and SO_2 detection limits with this analytical setup have been determined to be 1.0, 0.1 and 5.0 ppmv, respectively.

Kinetic experiments utilized mass spectrometry to analyze for O_2 , N_2 and H_2S gases at the reactor exit. For these experiments, gas chromatography did not possess the sampling time scale necessary to resolve initial rate kinetic data. The mass spectrometer used was a VG Prima 600™ 100 amu scanning magnetic sector mass spectrometer. Prior to kinetic rate testing, the activated carbon catalyst was reduced to an average particle diameter of 100 μm and was dried under vacuum at 50 $^\circ\text{C}$ to remove residual moisture. Potential sulfur sinks in the sampling system were eliminated prior to the beginning of each kinetic experiment by flushing the sample lines with 0.1 vol% H_2S until inlet concentrations equaled the exit concentrations. H_2S , N_2 and O_2 readings were reproducible over the course of a run, indicating that mass spectrometer drift and continuing sulfur saturation in either the reactor or the reactor by-pass were not significant factors. Sensitivity limits for the mass spectrometer were determined to be approximately 1.0 ppmv for H_2S , O_2 and N_2 .

The catalyst samples were analyzed for intraparticle sulfur diffusion profiles utilizing electron dispersive spectrometry. A Noran micro-z energy dispersive spectrometer detector, interfaced with a Noran 8502 switching system that was equipped with a PAC 5000 automation system

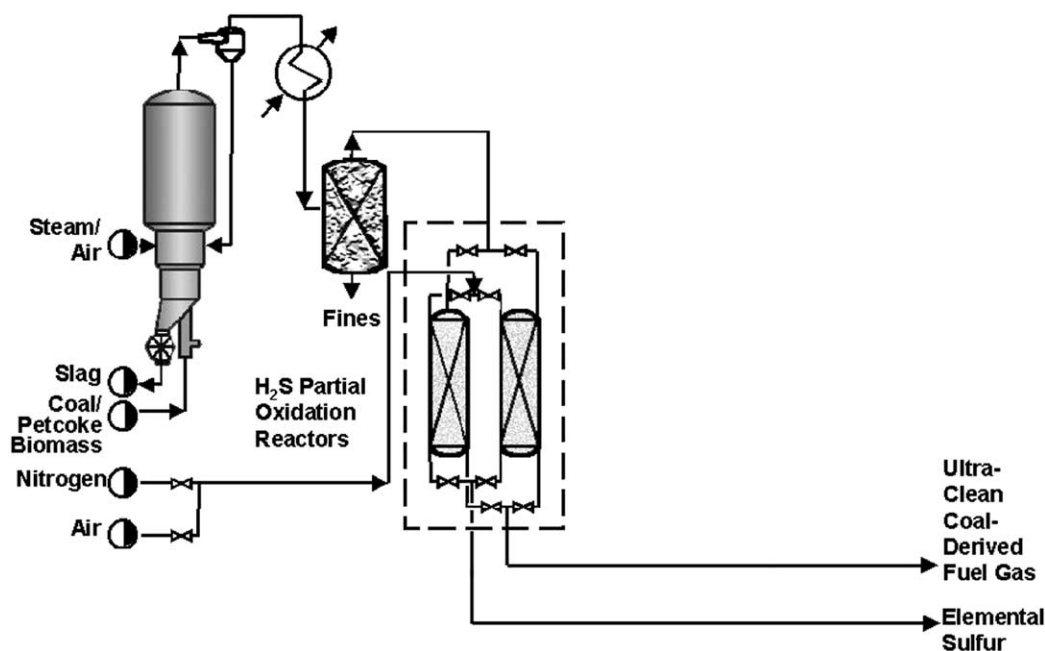


Fig. 2. Integration of H₂S catalytic partial oxidation technology into an integrated gasification combined cycle fuel cell power plant.

attached to a JOEL, Model 840A scanning electron microscope was used. Detector resolution as measured by the Mn K α spectral line was 151 keV.

Powder X-ray diffraction (XRD) of crystalline sulfur loaded in the catalyst particles was performed using an APD1700 automated powder diffractor system 1, utilizing nickel filtered Cu K α radiation. Generator settings were 50 kV and 30 mA. Samples were scanned from the Bragg angle, 4–90° 2 θ , at a constant scanning speed of 1 degree per second and a step size of 0.015°.

3. Results and discussion

3.1. Coal-derived synthesis gas desulfurization

H₂S catalytic partial oxidation technology integrated into a coal-fired fuel cell power plant would replace the liquid amine scrubber desulfurizer, the zinc polishing unit and the multi-stage Claus plant. Thermally, the two technologies operate at similar temperatures. However, H₂S catalytic partial oxidation technology possess the added benefit of combined acid gas separation and conversion to elemental sulfur within a single step, and without the need for regeneration of the amine solution. This integration is shown in Fig. 2.

Fuel gases derived from coal gasification are rich in H₂, CO, water vapor and contain sulfur in the form of H₂S. A typical Texaco entrained O₂-blown coal-derived fuel gas is given in Table 2, where the H₂S content has been normalized to 0.1 vol%. In this series of experiments, the ability of activated carbon to catalyze H₂S present in a coal-derived synthesis gas directly to elemental sulfur was

assessed. H₂S removal efficiency and the extent to which side reactions occur as a function of temperature are examined through a series of planned runs. Each run was timed to last 6 h with each run taking place at a different temperature: 135, 145, 155, 165 and 175 °C.

Fig. 3 shows the ability for this catalyst to consistently remove H₂S levels down to below 1.2 ppmv. The experiments were conducted with an H₂S/O₂ ratio of 1:5. The addition of excess oxygen was necessary to minimize the side reaction between CO and sulfur vapor to form COS. At these conditions any excess O₂ passed through the carbon bed unreacted. Fig. 4 shows that as the O₂/H₂S ratio is increased, the COS level drops indicating that it is surface bound carbon monoxide (CO*) that is reacting with sulfur to form COS. From Fig. 5, a strong functionality of COS

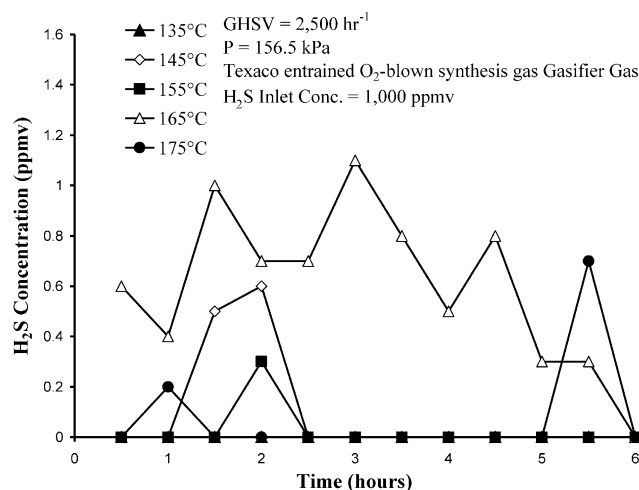


Fig. 3. The effect of temperature on H₂S removal efficiency during H₂S catalytic partial oxidation of a Texaco O₂-blown gasifier gas.

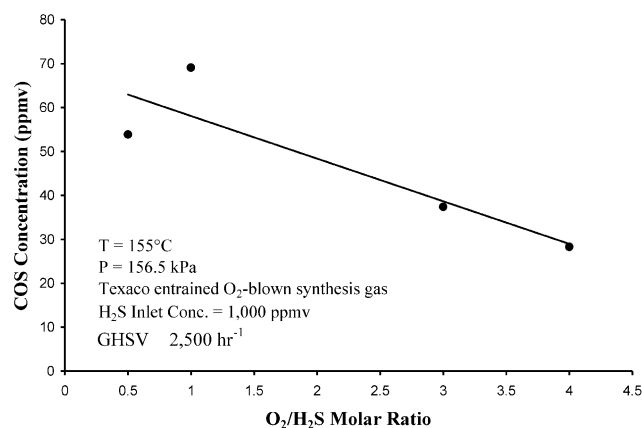
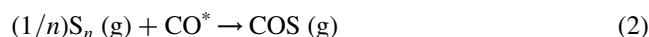
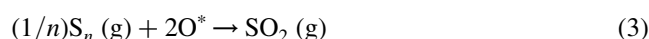


Fig. 4. The effect of O₂ to H₂S ratio on COS formation during H₂S catalytic partial oxidation of a Texaco O₂-blown gasifier gas.

formation with temperature is observed. This is a strong indication that vapor phase sulfur was reacting with the CO* to form COS. Thus, the formation of COS occurs via the reaction:



Another undesirable reaction that occurs is the over-oxidation of sulfur resulting in the formation of SO₂. Fig. 6 shows that elemental sulfur trapped within the pores of the catalyst may be over-oxidized to SO₂ at temperatures above 155 °C. Above 155 °C, and as reaction exposure time increases, SO₂ formation also increases. This indicates that as the smaller pores are filled first, the vapor pressure of the sulfur product increases with increasing pore size. The sulfur vapor then reacts with surface bound oxygen (O*) to form SO₂. Thus, the formation of SO₂ occurs via the reaction:



Clearly, the benefit derived from H₂S selective catalytic partial oxidation technology is that H₂S separation and conversion to elemental sulfur occur within a single process

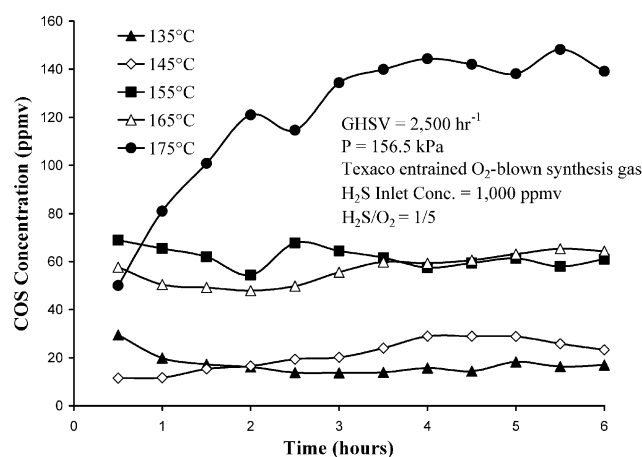


Fig. 5. The effect of temperature on COS formation during H₂S catalytic partial oxidation of a Texaco O₂-blown gasifier gas.

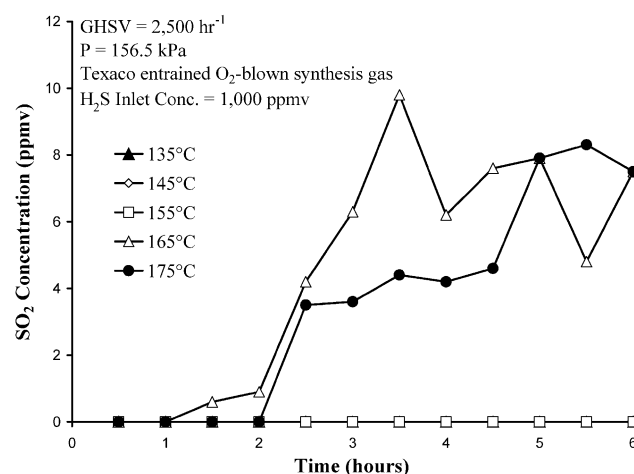


Fig. 6. The effect of temperature on SO₂ formation during H₂S catalytic partial oxidation of a Texaco O₂-blown gasifier gas.

step. At its present state, this technology is suitable as a bulk hydrogen sulfide remover from coal-derived synthesis gases and is much less energy intensive than an amine based process. Continued catalyst development is required before a COS shift reactor and zinc oxide guard bed could be eliminated for certain applications.

3.2. Liquid fuel desulfurization

H₂S catalytic partial oxidation technology integrated into a fuel cell system with a liquid middle distillate fuel processor, would directly replace the zinc oxide sorbent bed. Hydrodesulfurization, to convert the organic sulfur compounds into H₂S, would likely be necessary. However, H₂S catalytic partial oxidation would replace a bulky batch wise operation with a continuous one. Fig. 7 is a schematic of an internally reforming solid oxide fuel cell coupled with a continuous H₂S catalytic partial oxidation desulfurization system. In this system, some H₂ produced from the reformer is utilized as H₂ makeup. The bulk of the H₂ recycles from the H₂S catalytic partial oxidation unit, after most of the sulfur is removed, back to the hydrodesulfurizer. A typical hydrodesulfurizer effluent for this fuel processor after processing NATO F-76 naval distillate fuel contains 78 vol% H₂, up to 20.5 vol% N₂ and up to 1.5 vol% H₂S. Complete removal of H₂S at this stage is unnecessary since the hydrodesulfurization catalyst must be maintained in a sulfide state.

In this series of experiments, activated carbon was tested for its ability to catalyze H₂S directly into elemental sulfur while in the presence of a simulated hydrodesulfurizer effluent stream. H₂S removal efficiency and the extent to which side reactions occur as a function of temperature were examined. Each run was timed to last 6 h with each run taking place at a different temperature: 145, 155 and 165 °C. The H₂S/O₂ ratio was 1:1/2. Details of the stream composition used are given in Table 2.

From Fig. 8, the H₂S concentration at the reactor exit

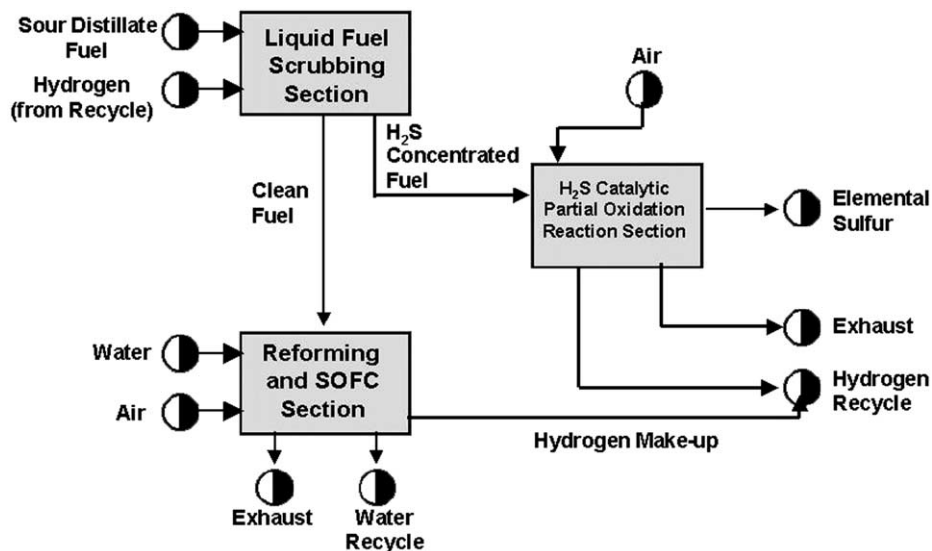


Fig. 7. Integration of H₂S catalytic partial oxidation technology into a liquid middle distillate fuel processor and SOFC power plant.

continually rises for the first hour of operation. At the end of this period of time, the catalyst reached an equilibrium activity level, where the sulfur product must leave the catalyst surface to renew active sites. It is this active site occlusion that is responsible for the decline in activity and H₂S removal efficiency. And though H₂S carryover was taking place, at these conditions any excess O₂ simply passed through the carbon bed unreacted. In addition, COS, CH₄ and CO₂ evolution were not observed. Fig. 9 shows that some SO₂ evolution is taking place after the first hour of operation. The mechanism for this SO₂ formation is consistent with that proposed in reaction (3).

3.3. Natural gas desulfurization

Pipeline natural gas contains any number of sulfur odorants in addition to trace amounts of H₂S. Catalytic partial oxidation may be integrated into natural gas fuel

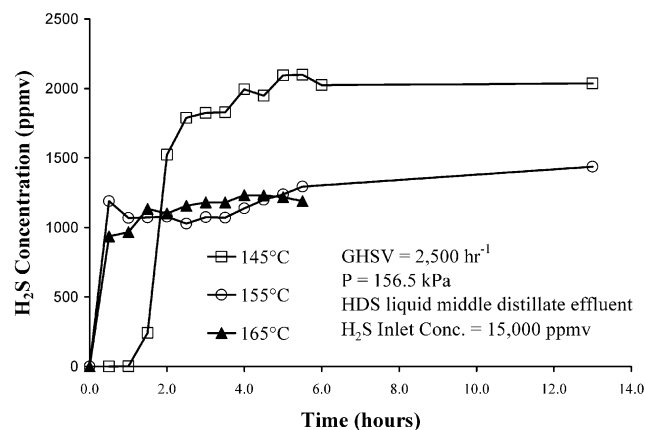


Fig. 8. The effect of temperature on H₂S removal efficiency during H₂S catalytic partial oxidation of sour liquid middle distillate hydrodesulfurizer effluent.

processors to save footprint and to provide for continuous sulfur removal, theoretically, to part-per-billion levels. Fig. 10 is a schematic of an H₂S catalytic partial oxidation fuel processor for natural gas fuel cell power plants. Like the liquid middle distillate system, some H₂ produced from the reformer must be recycled back to the hydrodesulfurization reactor. Though in this case, the H₂ partial pressure need not be as substantial.

In this experiment, a gas mix comprised of 99.95 vol% CH₄ and 0.05 vol% H₂S was utilized to simulate effluent from a natural gas hydrodesulfurizer. Details of this stream composition are given in Table 2. The sulfur level here was exaggerated to make changes in catalyst performance readily discernable on a shorter time scale. Sufficient air was injected to achieve an H₂S/O₂ ratio of 1:2. The results demonstrated that methane co-oxidation did not take place under these conditions. H₂S levels were consistently removed to 0.0 ppmv over the temperature range 135–175 °C. From Fig. 11, SO₂ evolution became significant after 1–2 h of operation at all temperatures. This is

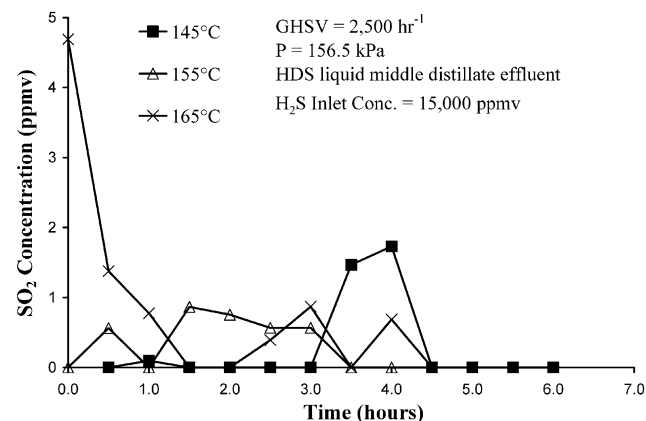


Fig. 9. The effect of temperature on SO₂ formation during H₂S catalytic partial oxidation of sour liquid middle distillate hydrodesulfurizer effluent.

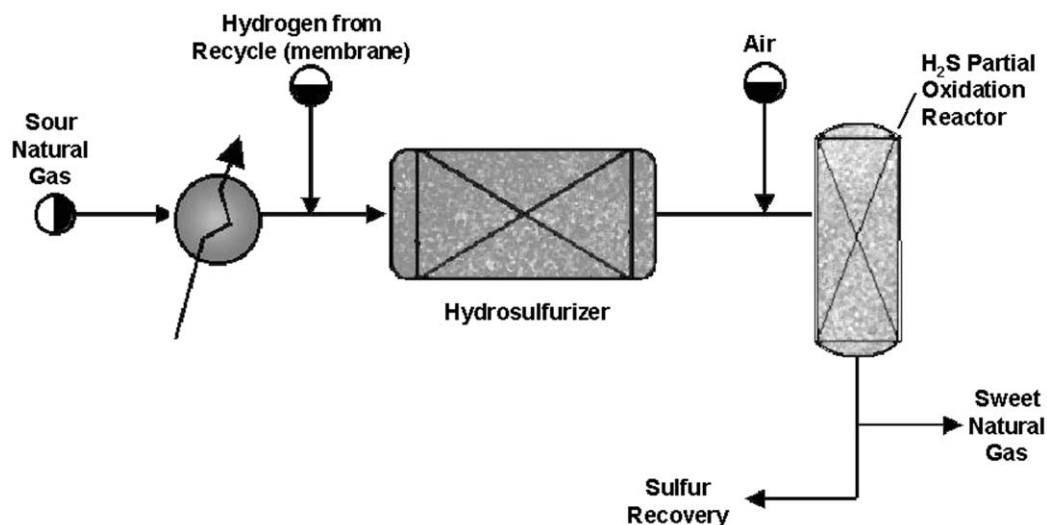


Fig. 10. Integration of H₂S catalytic partial oxidation technology into a sour natural gas fuel processor.

consistent with proposed mechanism in reaction (3). Clearly, for fuel cell systems operating on natural gas, SO₂ breakthrough will have to be considered in addition to H₂S.

3.4. Reaction rate analysis

Numerous kinetic and mechanistic investigations of H₂S selective catalytic oxidation have been reported in the literature. Of particular interest as a catalyst has been activated carbon due to its favorable kinetics at low temperatures, its high surface area and microporous structure, and its low cost. Table 3 is a compilation of kinetic parameters by numerous investigators who have studied H₂S catalytic partial oxidation over activated carbon. From this table, considerable disparity in the reported kinetic order and activation energy for this reaction exists.

Reported activation energies for this reaction over activated carbon range from 20.1 to 37 kJ/g mol. The

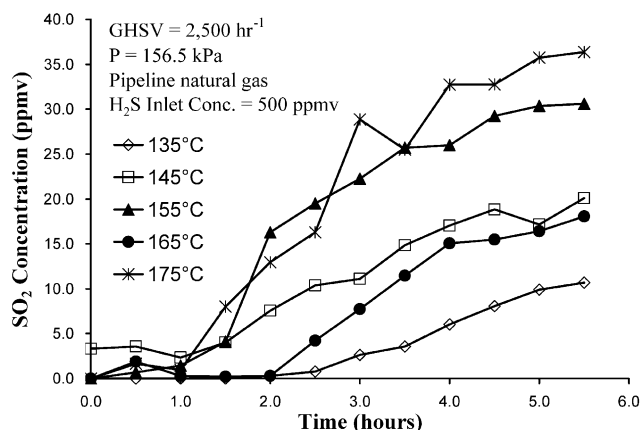


Fig. 11. The effect of temperature on SO₂ formation during H₂S catalytic partial oxidation of sour natural gas.

kinetic order ranges from 0 to 1, for H₂S, and from 0.1 to 1, for O₂. The earliest kinetic measurements were performed by Puri et al. [12] who made the important observation that active sites were occluded by the presence of product sulfur, which became fixed in the activated carbon pores. Steijns and Mars [13] observed an initial increase in the reaction rate followed by a decrease in activity and concluded that this reaction was autocatalytic. Later, Sreeramamurthy and Menon [14] conducted experiments on elemental sulfur and concluded that elemental sulfur had no catalytic effect on this reaction. They also concluded that the active mechanism was the chemisorption of both H₂S and O₂ on the activated carbon surface, followed by a rate controlling surface reaction. Cariso and Walker [15] showed that oxygen is chemisorbed and that the rate controlling reaction is between O* and gas phase H₂S via the Mars–Van Kremlin mechanism.

From the existing literature, it is not possible to prefer any one kinetic expression or mechanism. Therefore, for comparative purposes, we undertook similar kinetic measurements in our laboratory. For this series of experiments, the H₂S concentration was varied independently from the O₂ concentrations used. The H₂S concentrations used were 250, 500, 1000 and 3000 ppmv and O₂ concentrations were half, two and five times the H₂S levels. The temperatures studied were 145, 155, 165 and 175 °C. The particle size was reduced to 100 μm and the method of initial rates was employed to ensure that the kinetic measurements were free from intraparticle resistances. External mass transfer resistances were minimized by incrementally increasing the superficial gas velocity through the reactor, at constant residence time, until a plot of conversion versus superficial gas velocity yielded a zero slope. The superficial gas velocity used for all experiments was 0.2 m/s (STP). A catalyst weight to inlet flow ratio, $W/F = 6.2 \times 10^{-5}$ g catalyst/(std. cm³ min⁻¹) was kept constant throughout these experiments. This ensured that

Table 3
Kinetic parameters for H₂S catalytic partial oxidation over activated carbon

Contacting mode	Model	Temp. range (°C)	E _A (kJ/g mol)	Ref.
PF, 10.0 g	PL, $n = 0, m = 0.1$	120–240	25.1	[12] ^a
Diff.	MVK, $n = 1.0, m = 0.5$	70–100		[14]
Diff., 84 μm	PL, $n = 1.0, m = 0$	100–160	20.1	[15]
Diff., 25–100 mg	Redox, $n = 0.5, m = 0$ (O ₂ > 35 vol%) and $m = 0.85$ (O ₂ < 35 vol%)	130–200	$E_{ox} = 37\text{V}4,$ $E_{red} = 52\text{V}5$	[13,16]
PF, 630 μm	PL, $n = 0.5, m = 0$	24–200	23.9	[17]
Diff.	MVK, $n = 1, m = 0.5$	40–80	–	[18]
Diff., 0.063 mm	LHHW, $n = 1.0, m = 0.5$	125–200	23.6	[6]
PF	LHHW, $n = 1.0, m = 0.5$	125–200	34.2	[4]

LHHW, Langmuir–Hinshelwood–Hougen–Watson; PL, power law; MVK, Mars–Van Kremlin; n, order in H₂S; m, order in O₂; Diff., differential reactor; PF, plug flow reactor.

^a Calculated by Steijns et al. (1976).

H₂S conversions were kept to less than 15.0% and an absence of external concentration gradients. Under these conditions the following equation is valid for the reaction rate:

$$-r_{H_2S} = \frac{(C_{H_2S,i} - C_{H_2S,e})}{w} Q \quad (4)$$

where $C_{H_2S,i}$ was the inlet H₂S concentration, $C_{H_2S,e}$ was the reactor exit H₂S concentration, Q was the volumetric flow rate and w was the mass of the activated carbon catalyst tested. The power law rate model for reaction (1) may be written as:

$$-r_{H_2S} = k e^{-E_A/RT} C_{H_2S}^n C_{O_2}^m \quad (5)$$

Eq. (5) was then linearized so that a linear least squares approach could be employed to solve for the activation energy, E_A , and the reaction orders in H₂S, n , and O₂, m :

$$\ln(-r_{H_2S}) = \ln(k) - \left(\frac{E_A}{R}\right) \frac{1}{T} + n \ln(C_{H_2S}) + m \ln(C_{O_2}) \quad (6)$$

A linear least squares fit of Eq. (6) yielded an activation energy of $E_A = 34.4$ kJ/g mol. The reaction order in H₂S was determined to be 1.0 and 0.3 in O₂. And the rate

constant was determined to be 6.769×10^9 (cm³)^{1.3}/(mol^{0.3} g catalyst min). Fig. 12 is a comparison of the power law model to the experimental data and shows the goodness of fit. A correlation coefficient of 0.97 was obtained. A reaction order of 1.0 in H₂S is indicative of adsorption control. The reaction order in O₂ of 0.3 indicates a more complex rate controlling mechanism for O₂ than simple adsorption.

3.5. Electron probe microanalysis

Fig. 13(a) is an electron dispersion spectroscopic (EDS) analysis of a cross-section of activated carbon catalyst pellet that was exposed to 0.1 vol% H₂S with a stoichiometric amount of O₂ at 175 °C for 8 h. The sulfur profile, indicated by white, within the pellet is that of a sharp interface. This indicates that the reaction is diffusion controlled, with the reaction taking place significantly faster than reactant diffusion and adsorption onto active sites. Fig. 13(b) is an EDS analysis of a cross-section of activated carbon catalyst that was exposed to 0.1 vol% H₂S with a stoichiometric amount of O₂ at 175 °C for 16 h. It illustrates that the interior of the pellet remains accessible even through saturation.

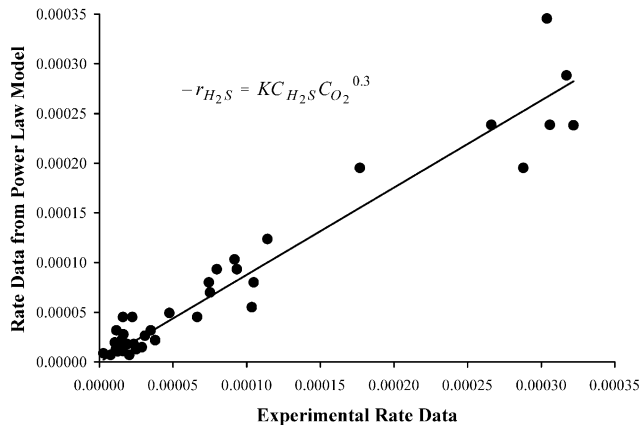


Fig. 12. Comparison of model and experimental data.

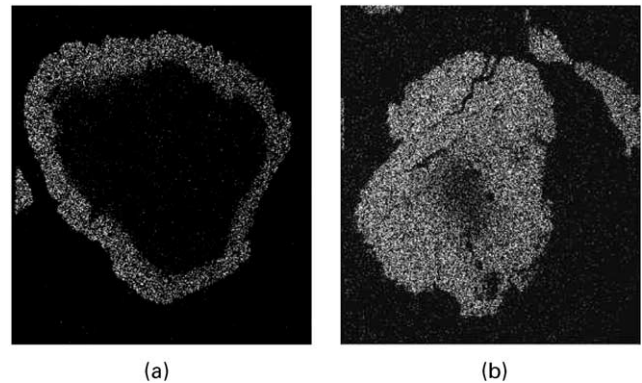


Fig. 13. (a) Partially saturated activated catalyst pellet. (b) Fully saturated activated carbon catalyst pellet.

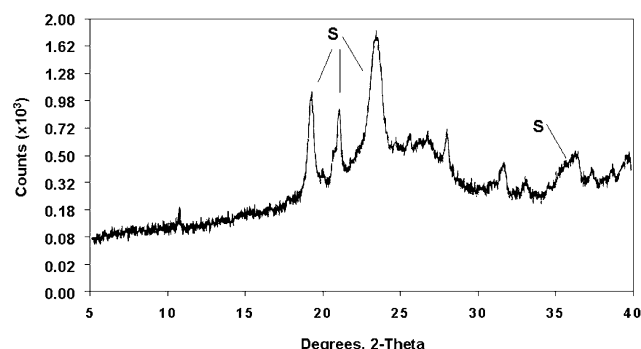


Fig. 14. Powder XRD pattern of a fully saturated activated carbon catalyst pellet.

3.6. Powder XRD analysis

Powder XRD analysis was carried out on activated carbon catalyst that was exposed to 0.1 vol% H_2S with a stoichiometric amount of O_2 at 175°C for 16 h. This analysis was conducted in order to verify that the product within the catalyst pores is elemental sulfur. Fig. 14 is the XRD pattern indicating that crystalline sulfur is present. Peak locations of 19.0° , 20.9° , 23.2° and 36.4° correspond to crystalline sulfur. The broadness of the peaks, however, preclude an exact determination of the crystalline form, monoclinic or rhombohedral.

4. Conclusions

H_2S catalytic partial oxidation technology has been shown to be highly integratable into fuel cell power plant applications. This technology possesses the ability to continuously oxidize H_2S to elemental sulfur from hydrocarbon feedstocks. In coal-derived synthesis gas, the activated carbon catalyst was able to reduce total sulfur ($\text{H}_2\text{S} + \text{SO}_2 + \text{COS}$) levels to below 20 ppmv at temperatures less than 145°C . Above 145°C , the sulfur product began to over-oxidize and COS formation became significant. It was also demonstrated that COS levels could be reduced by increasing the $\text{O}_2/\text{H}_2\text{S}$ ratio. This indicated that with competitive adsorption taking place, the activated carbon catalyst possessed a greater affinity for O_2 than CO.

In middle distillate fuel processing systems, the activated carbon catalyst demonstrated a high sulfur selectivity. Continuous operation was achieved, where the sulfur product was continuously being wicked away from the catalyst surface. On average, 90% of the H_2S was converted to elemental sulfur leaving some residual O_2 . Some over-oxidation of sulfur product did occur.

In natural gas fuel processing systems, H_2S selective catalytic partial oxidation technology using activated carbon as a catalyst has the ability to remove H_2S to less than 1.0 ppmv. Over-oxidation of the sulfur product over time did occur and correlated with sulfur loading.

The reaction rate data that was reported in many earlier studies appeared to be influenced by non-intrinsic reaction rate phenomena. Our laboratory determined the activation energy for this reaction to be 34.4 kJ/g mol with a reaction order in H_2S of 1.0 and 0.3 in O_2 .

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